Time: 2 hours

Chemistry 228

February 12, 1998

Final Exam

Name:
Number:

$R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$
$h = 6.63 \times 10^{-34}\ J\ s$
$c = 3 \times 10^{8}\ m\ s^{-1}$
$R_H = 109678\ cm^{-1} = 2.18 \times 10^{-18}\ J$
$m_e = 9.11 \times 10^{-31}\ kg$
$e = 1.60 \times 10^{-19}\ C$
First Bohr radius for H: $r = n^2h^2/Z4\pi^2m_ee^2 = a_0 = 0.529\ Å$
Energy of a Bohr orbit: $E = -2\pi^2m_ee^4Z^2/h^2n^2$

1. Using molecular orbital theory, determine the bond order, number of unpaired electrons and write the electronic configuration of the following molecules:

   a. C_2

   b. N_2^-

   c. O_2

   d. F_2^-

2. The spectrum of He^+ contains, along with many others, lines at 329,170 cm^{-1}, 399,020 cm^{-1}, 411,460 cm^{-1} and 421,330 cm^{-1}. Show that these lines fit a Rydberg-type equation, $\nu = R(1/n_1^2 - 1/n_2^2)$. What is the ratio of R_H to R_{He^+}? Do these facts agree with Bohr's theory of hydrogenlike atoms?

3. An atom is observed to emit light at 1000 Å, 1250 Å and 5000 Å. Theoretical considerations indicate that there are only two excited states involved. Explain why three lines are observed. How far in energy are the excited states above the ground state?

4. For each of the following cases give the Lewis structure of a known chemical example:
   a. a diatomic molecule with one unpaired electron

   b. a triatomic molecule with two double bonds

   c. an alkaline-earth oxide

   d. a diatomic molecule with formal charge separation

   e. a molecule or ion with two equivalent resonance structures

   f. a molecule or ion with three equivalent resonance structures

5. The atoms of the yet-to-be-discovered "hypotransition" elements, starting at Z = 121, will have electrons in the 5*g* orbitals.

   a. How many elements will there be in the hypotransition metal series?

   b. How many of the atoms will be diamagnetic?

   c. Which electronic configurations in the series will have seven unpaired electrons?

   d. What is the maximum number of unpaired electrons an atom can have in the series? Will this be a new record for atoms in the periodic table?

   e. What is the ionization energy (*IE*) of an electron in a 5*g* orbital of atomic hydrogen? Is this likely to be larger, or smaller, than the *IE* of a 5*g* electron in one of the hypotransition elements? Briefly explain your choice.

   f. In atomic hydrogen the 5s, 5p, 5d, 5f, and 5g orbitals all have the same energy. Will this be true for the hypotransition elements? If not, what will the energy order be? Explain briefly.

6. The electronic structure of the thiocyanate ion, NCS^-, can be represented as a hybrid of two resonance structures. Write these two structures and give the C-N and C-S bond orders for each structure.

7. Use VSEPR theory to predict the molecular shapes of XeF_4, XeO_4, XeO_3 and XeF_2. Determine the point group of each molecule.

8. Give the orbital hybridization of the central atom and the VSEPR-theory geometrical structure for AsH_3, ClF_3 and $SeCN^-$.

9. Consider a compound with the molecular formula $Fe(CO)_3(PF_3)_2$.
   a. Draw all possible isomers of this compound, assuming trigonal bipyramidal geometry; assign a point group for each of these isomers.

   b. How many IR-active CO stretching bands should each isomer display?

10. Describe the crystal structures of rock-salt and perovskite in detail. Give two examples each of compounds with such structures.

11. a. Complete the following table.

crystal structure	**packing (e.g. fcc,hcp,bcc)**	**coordination (e.g. (6,6))**	**examples of compounds**
cesium chloride			
zinc blende			
fluorite			
antifluorite			
wurtzite			
nickel-arsenide			
rutile			

b. Use the radius ratio table to predict a crystal structure for the following compounds. Explain.

coordination number of smaller ion	radius ratio ($r_</r_>$)
8	> 0.7
6	0.4 – 0.7
4	0.2 – 0.4
2	0.1 – 0.2

1. BeS (r_{Be2+} = 0.59 Å; r_{S2-} = 1.70 Å)

2. K_2O (r_{K+} = 1.52 Å; r_{O2-} = 1.26 Å)

3. SnO_2 (r_{Sn4+} = 0.83 Å)

12. Give the approximate pk_a values for the following acids (use Pauling's rules).

a. H_3PO_3 pk_1 = pk_2 =

b. H_2SO_4 pk_1 = pk_2 =

c. $HClO_4$ pk_1 =

d. H_5IO_6 pk_1 = pk_2 =

13. Identify the acids and bases in the reactions:

    a. $FeCl_3 + Cl^- \rightarrow [FeCl_4]^-$

    b. $I^- + I_2 \rightarrow I_3^-$

    c. $[:SnCl_3]^- + (CO)_5MnCl \rightarrow (CO)_5Mn\text{-}SnCl_3 + Cl^-$

14. Explain the classification of hard/soft acids/bases and give two examples for each.

15. Silver perchlorate, $AgClO_4$, is significantly more soluble in benzene than in alkane solvents. Account for this observation in terms of Lewis acid/base properties.

16. What was Victor Gutmann's contribution in the field of acids and bases?

17. Calculate the lattice enthalpy of magnesium bromide from the following data:

	ΔH^0 (kJ/mol)
Sublimation of Mg(s)	+148
Ionization of Mg(g) to Mg^{2+}(g)	+2187
Vaporization of Br_2(l)	+31
Dissociation of Br_2(g)	+193
Electron attachment to Br(g)	-331
Formation of $MgBr_2$(s)	-524